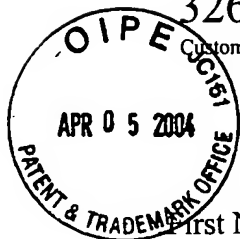


32692

Customer Number

Patent  
Case No.: 58011US004



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

First Named Inventor: SAITOH, TSUNEYOSHI

Application No.: 10/658656

Group Art Unit: 1712

Filed: September 9, 2003

Examiner: Unknown

Title: WATER-REPELLENT SHEET WITH PROTECTIVE FILM, SHEET FOR  
PREVENTING SNOW ADHESION AND METHOD FOR PRODUCING WATER-  
REPELLENT BOARD

**SUBMISSION OF TRANSLATION**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**CERTIFICATE OF MAILING**

I hereby certify that this correspondence is being deposited with the United States Postal Service as First Class Mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on:

1 April 2004  
Date

Amber Nicholson  
Signed by: Amber Nicholson

Dear Sir:

Further to the Information Disclosure Statement mailed February 16, 2004, please find enclosed the translation of JP 10-138416.

Respectfully submitted,

MARCH 31, 2004  
Date

By: James D. Christoff  
James D. Christoff, Reg. No.: 31,492  
Telephone No.: (651) 733-1512

Office of Intellectual Property Counsel  
3M Innovative Properties Company  
Facsimile No.: 651-736-3833

Japan Patent Office (JP)

LS # 51

## Public Report of Opening of the Patent

Opening No. of patent: H10-138416

Date of Opening: May 26, 1998

Int.Cl.	Distinguishing mark	F1	
B 32 B 27/30		B 32 B 27/30	D
27/18		27/18	Z
C 08 J 7/04	CEW	C 08 J 7/04	CEWS CEWZ

Request for examination: requested

Number of claim requested: 2 OL

-----  
 ----

Application of the patent: No. H 8-302745

Date of application: Nov. 14, 1996

Applicant: Seon Co. Ltd.

4-34, 1-chome, 1, Kikusuimotomachi, Shiraishi-ku, Sapporo-shi, Hokkaido, Japan

Applicant: Dainippon Shikizai Manufacturing Co Ltd.

7-1, 3-chome, New Kudan Bldg., Kanda Jinbocho, Chiyoda-ku, Tokyo, Japan

Applicant: Mitsunori Yoshida

Hokkaido Manufacturing Test Place, 1, 11-chome, 19-jo nishi, Kita, Kit-ku,

Sapporo-shi, Japan

Applicant: Science Technology Promotion Enterprise

1-8, 4-chome, Honmachi, Kawaguchi-shi, Saitama, Japan

Inventor: Hiromi Sekiguchi

Seon Co. Ltd., 4-34, 1-chome, 1, Kikusuimotomachi, Shiraishi-ku, Sapporo-shi,

Hokkaido, Japan

Inventor: Katsuo Kobayashi

Dainippon Sikizai Manufacturing Co Ltd., Sanwa Plant, 1778, Owada Sezaki,

Sanwacho, Sarushima-gun, Ibaragi, Japan

Inventor: Mitsunori Yoshida

Hokkaido Manufacturing Test Place, 1, 11-chome, 19-jo nishi, Kita, Kit-ku,

Sapporo-shi, Japan

Assigned representative: Shigemitsu Sasaki, patent attorney



## Detailed Report

### (Name of invention)

Adhesive film for preventing accumulation of snow and ice

### Abstract

#### (Object)

The object of this invention is to offer an adhesive film for preventing accumulation of snow and ice with the following features. The film can be applied in any weather, and it requires no special skills. It is effective even at low temperatures from 0°C to -10°C. It is easy to remove and reapply or repair.

#### (Solution)

This invention has the following characteristics: The construction of this adhesive film for preventing accumulation of snow and ice is as follows: first, a layer to prevent accumulation of snow and ice is formed on the front surface of the plastic. Then a releasable adhesive layer and mold-release sheet are formed on its back surface. In this film, the layer to prevent accumulation of snow and ice has the following composition. It is a mixture of specific fluorine based co-polymers and acryl base resin dissolved and mixed in an organic solvent. At least one kind of hydrophobic organic substance selected from nonionic based surfactants, fluorine based surfactants, low molecular weight tetrafluoro ethylene polymer powders, or silicon bases resin powder is added to this mixture in a specific amount.

#### (Effect)

The above problems can be solved by using this invention.

### Sphere of the patent application

#### (Claim 1)

Claim 1 is concerning an adhesive film for preventing accumulation of snow and ice which has the following characteristics: The construction of this adhesive film for preventing accumulation of snow and ice is as follows: first, a layer to prevent accumulation of snow and ice is formed on the front surface of the plastic. Then a releasable adhesive layer and mold-release sheet are formed on its back surface. In this film, the layer to prevent accumulation of snow and ice has the following composition. First, a mixture of resins which can be dissolved in organic solvent is prepared. It is 40 to 80 wt. % fluorine based co-polymer resin which consists of monomers of vinylidene fluoride, tetrafluoroethylene, and hexafluoropropylene, and 60 to 20 wt. % acryl based resin which contains methyl methacrylate. These are necessary components in this resin mixture. 0.1 to 200 wt. parts of at least one hydrophobic organic substance selected from nonionic based surfactants, fluorine base surfactants, low molecular weight tetrafluoro ethylene polymer powders, or silicon based resin powders is added to 100 wt parts of this mixture to form the layer.

(Claim 2)

Claim 2 is concerning the adhesive film for preventing accumulation of snow and ice in claim 1 where the releasable adhesive has 10 g/25 mm to 1000 g/25 mm adhering strength.

Detailed explanation of this invention

[0001]

(Field that this invention belongs to)

This invention is concerning an adhesive film for preventing accumulation of snow and ice. In more detail, it is concerning an adhesive film which is applied to structures in cold climates where snow or ice must not be deposited. This can prevent accumulation of snow and ice and also can be removed easily and reapplied or repaired.

[0002]

(Prior art)

In cold, snowy areas, snow and ice deposits cause various problems to daily life or industry. For instance, power could be lost due to ice deposits on electric wiring. When snow accumulation is intense, towers for electric wires may collapse and cause power outages over a wide area. Snow which is blown up by high speed trains becomes attached to pantographs or the lower portion of vehicles and causes problem driving the train. In addition, it can prevent accidents due to snow falling from structures such bridges, iron towers, buildings, houses; maritime perils due to accumulation of ice on ships; airplane accidents due to accumulation of ice on aircraft; communication problems due to accumulation of ice and snow on electric communication facilities; and traffic jams or accidents due to accumulation of snow on road signs, signal lights, etc. These types of events sometimes affect human life. Technology which prevents accumulation of snow and ice on various structures is in strong demand in cold, snowy areas.

[0003] The phenomenon of snow and ice accumulation in the natural world has different mechanisms depending on temperature, wind speed, sunlight, etc. However, based on studies, attaching of wet snow to objects is due to the surface tension of water contained in the snow. Attaching of dry snow to objects is due to the fact that an ice bond is formed between the snow and the object. In other words, snow and ice accumulation on the surface is regarded as hydrogen bonding between hydrogen molecules and atoms on the surface, or van der Waals forces. Accordingly, to prevent snow and ice from attaching to the surface of an object, you can lower the bonding between water molecules and the surface of the object, increase the wetting angle, or decrease the free energy of the surface of the object.

[0004] Until now, the following methods of preventing accumulation of snow and ice on the surface of structures have been suggested. Objects can be coated with a special paint which prevents ice and snow from depositing on the surface of structures. (refer to Japan patent No. S 59-25868, No. S 61-23656, No. H 7-331122). However, forming a flat, smooth, and uniform coating on the surface requires high skill. Not only that, it also depends on weather such as temperature, humidity, rain, or snow, and the time of day when work can be done is limited in many cases. In addition, when the coating is

exposed to weather for a long time, deterioration cannot be avoided. Reapplication or repair requires a long time and it involves a lot of work.

[0005] Another method of preventing accumulation of snow and ice has been suggested. First, a layer to prevent accumulation of snow and ice is formed on the front surface of a base sheet. The back side is covered with a pressure-sensitive adhesive layer and mold-release paper. When it is applied to a site where accumulation of snow and ice is to be prevented, the pressure-sensitive adhesive layer is exposed by removing the mold-release paper, and the pressure-sensitive adhesive layer is attached to the desired site. For instance, Japan patent No. H 2-145673 describes a layer which prevents accumulation of snow and ice which is coated with a substance that consists of (1) a copolymer which has fluoro olefin and a vinyl monomer with a hydroxyl group that can be co-polymerized with this fluoro olefin, (2) a silicon compound which has a group that reacts with the reactive group of copolymers of (1) or hydroxyl groups, (3) a polyisocyanate compound. In use, the mold-release paper is removed, and it is attached on a predetermined spot on the object.

[0006] However, though the adhesive sheet with a layer which prevents accumulation of snow and ice in Japan patent No. H 2-145673 is effective at low temperatures around  $-10^{\circ}\text{C}$ , it is not effective at around  $0^{\circ}\text{C}$ . The range of temperatures where it is effective is narrow. In addition, the pressure-sensitive adhesive layer on this adhesive sheet is strong and it cannot be removed. It is inconvenient when this adhesive sheet must be repaired.

[0007]

(Problem that this invention tries to solve)

The inventors of this invention made through research in order to offer technology which prevents accumulation of snow and ice which solves the above problems with the prior art. As a result, it was found that all of these problems can be solved by using a mixture of copolymers containing fluorine with a special composition and an acryl base resin to form a layer to prevent snow and ice from accumulating. A thin layer is formed on the surface of the substrate by mixing specific hydrophobic organic substances in the resin, and a removable adhesive is used on the back side of the substrate. These findings led to this invention.

[0008] That is, the object of this invention is as follows:

1. to offer an adhesive film to prevent accumulation of snow and ice which can be applied to the surface of various structures which is hardly affected by weather and can be applied without any special skill.
2. to offer an adhesive film to prevent accumulation of snow and ice which is effective over a wide temperature range from  $0^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$ .
3. to offer an adhesive film to prevent accumulation of snow and ice which is easily removed for reapplication or repair.

[0009]

(Steps for solution)

In order to solve the above problems, this invention offers an adhesive film for preventing accumulation of snow and ice which has the following characteristics: First, a layer to prevent accumulation of snow and ice is formed on the front surface of plastic.

Then a releasable adhesive layer and mold-release sheet are formed on its back surface. In this film, this layer to prevent accumulation of snow and ice has the following composition. First, a mixture of resins which can be dissolved in organic solvent is prepared. It has 40 to 80 wt. % fluorine based co-polymer resin which consists of vinylidene fluoride, tetrafluoroethylene, and hexafluoropropylene and 60 to 20 wt. % of acryl based resin which contains methyl methacrylate. These components are necessary. 0.1 to 200 wt. parts of at least one hydrophobic organic substance selected from nonionic based surfactants, fluorine based surfactants, low molecular weight tetrafluoro ethylene polymer powders, or silicon based resin powders are added to 100 wt. parts of this mixture to form the layer.

[0010]

(Embodiment of this invention)

In the following, this invention is going to be explained in detail. To make the adhesive film to prevent accumulation of snow and ice, a layer to prevent accumulation of snow and ice is first formed on the front surface of a plastic substrate. Then a removable adhesive layer and mold-release sheet are formed on its back surface. The plastic substrate is the base for the adhesive film for preventing accumulation of snow and ice. The layer to prevent accumulation of snow and ice is formed on the surface of substrate and prevents accumulation of snow and ice on the surface of the film. The function of the removable adhesive layer on the back side of the substrate is for attaching the film to structures where accumulation of snow and ice is to be prevented so that the film can be easily removed for repairs. The release sheet protects the adhesive layer.

[0011] The substrate should consist of synthetic resin with excellent chemical resistance with flexibility which will not be destroyed at extremely low temperatures. For example, there are films like polyethylene, polypropylene, ABS resin, AES resin, polyvinyl chloride, polyvinylidene chloride, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyamide, polyimide, etc. However, this synthetic resin is not limited to these examples only.

[0012] The manufacturing method of substrate film is not specifically limited. Any method such as T-dye extrusion, blow molding, calendaring, and casting can be used. The substrate film can be drawn, not drawn, transparent, or colored. Although the thickness depends on the structure to be protected, the area to be protected, etc., it should be in the range of 10 to 500  $\mu\text{m}$ . In this range, 30 to 120  $\mu\text{m}$  range is suitable.

[0013] In addition, a primer and corona discharging treatment or UV treatment can be administered to the surface of the film substrate to improve affinity with the layer to prevent accumulation of snow and ice, durability, etc. There is no specific restriction on the kind of primer, and you can use conventional ones based on polyurethane, titanate, polyethylene imine, etc. The thickness of the primer can be from 10 to 100 nm.

[0014] The layer to prevent accumulation of snow and ice on the surface of the substrate consists of a mixture of resins that can be dissolved in organic solvent that consists of 40 to 80 wt. % of fluorine based copolymer resin and 60 to 20 wt. % acryl based resin as necessary main components. If the amount of fluorine based copolymer resin in the resin mixture is less than 40 wt. %, weather resistance and pollution prevention drop. On the

other hand, if it exceeds 80 wt. %, bonding with the substrate and strength drop, and this is not desired.

[0015] The fluorine based copolymer resin should have vinylidene fluoride, tetrafluoroethylene and hexafluoro propylene as component monomers. The amount of tetrafluoroethylene monomer in the fluorine based copolymer resin should be from 20 to 40 wt. %. If it is less than 20 wt. %, the coating composition will not be uniform. On the other hand, if it exceeds 40 wt. %, mutual solubility with the acryl based resin drops. Either case is not desired. If the amount of hexafluoropropylene monomer in the fluorine based copolymer resin is more than 20 wt. %, the layer to prevent accumulation of snow and ice becomes too soft, which is not desired.

[0016] Any acryl base resin that contains methyl methacrylate can be used. Examples include homo polymers of methyl methacrylate monomers and copolymers which contain 90 wt. % or more methyl methacrylate monomer. If the amount of methyl methacrylate in the copolymer is less than 90 wt. %, mutual solubility with the fluorine based copolymer resin is reduced, which is not desired. Monomers which can be co-polymerized with the methyl methacrylate monomer include acrylic acid, methacrylic acid, ethylene, propylene, vinyl chloride, vinylidene chloride, vinyl acetate, 2-ethylhexyl acrylate, 2-hydroxy ethyl acrylate, 2-hydroxy ethyl methacrylate, hydroxy ethyl vinyl ether, etc. However, this invention is not limited to these examples only.

[0017] The fluorine based copolymer resin and acryl base resin above are dissolved in organic solvent to make a resin mixture. The organic solvent can be ketone group, ester group, or ether group. Specifically, there are methyl-n-propyl ketone, diethyl ketone, methyl isobutyl ketone, methyl-n-butyl ketone, ethyl-n-butyl ketone, cyclo hexane, n-propyl acetate, acetate-n-butyl, isobutyl acetate, methyl cellosolve, 2-methoxy-2-propanol cellosolve, etc. These organic solvents can be used either alone or in mixtures of two or more.

[0018] The amount of resin mixture that is dissolved in the organic solvent should be in the range that can be dissolved uniformly. If the amount of resin mixture is too small, it is difficult to form a layer to prevent accumulation of snow and ice with desired thickness. However, if the amount is too much, viscosity of the solution becomes high and it is difficult to form a uniform layer. The desired amount is as follows. The organic solvent should be 100 to 600 weight parts, preferably 200 to 400 weight parts per 100 weight parts of resin mixture.

[0019] At least one hydrophobic organic substance selected from nonionic surfactants, fluorine base surfactants, low molecular weight tetrafluoro ethylene polymer powders, and silicon based resin powders is added to the organic solvent solution above to make a mixture for forming the layer to prevent accumulation of snow and ice. These hydrophobic organic substances have functional groups with small critical surface energy in their molecular structure so they are hydrophobic and are effective in preventing accumulation of snow and ice.

[0020] Suitable nonionic surfactant include polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene sorbitan fatty acid ester, sorbitan fatty acid ester, etc. Suitable fluorine based surfactants include perfluoro alkyl carbonate, perfluoro alkyl ester phosphate, etc.



[0021] The low molecular weight tetrafluoroethylene polymer powder should have 1500 to 20000 average molecular weight measured by the melting point method and 0.1 to 20  $\mu\text{m}$  average particle diameter. One with less than 1500 molecular weight or more than 20000 molecular weight is not hydrophobic enough, and it is not effective in preventing accumulation of snow and ice. Low molecular weight tetrafluoroethylene polymer powders with less than 0.1  $\mu\text{m}$  or more than 20  $\mu\text{m}$  average particle diameter reduces hydrophobic properties, which is not desired.

[0022] The silicone base resin powder can be polysiloxane. Its average particle diameter should be 0.1 to 20  $\mu\text{m}$ . If its average particle diameter is less than 0.1  $\mu\text{m}$  or exceeds 20  $\mu\text{m}$ , hydrophobic properties are reduced, which is not desired.

[0023] The mixture of resins for forming the layer to prevent accumulation of snow and ice contains the hydrophobic organic substance above in the organic solvent solution of resin. The amount of hydrophobic organic substance should be in the range of 0.1 to 200 weight parts per 100 weight parts of resin mixture. If it is less than 0.1 weight part, it cannot improve hydrophobic properties of the layer to prevent accumulation of snow and ice. On the other hand, if it exceeds 200 weight parts, it is hard to form a uniform layer to prevent accumulation of snow and ice. The effects are best if the amount of hydrophobic organic substance is in the range of 0.5 to 100 weight parts.

[0024] To add the hydrophobic organic substance to the resin mixture dissolved in organic solvent used for forming the layer to prevent snow and ice from depositing, conventional devices for stirring and dispersing these substances such as a dissolver, steel ball mill, pebble mill, sand mill, etc., can be used.

[0025] In order to form the layer for preventing accumulation of snow and ice on the substrate film, the above mixture is applied on the surface of the substrate film and the organic solvent is removed by flashing. Conventional application method methods such as spraying, roll coating, immersion, curtain coating, etc., can be used. In order to flash the organic solvent from the coating, it can be heated and dried. For example, there are conventional methods such as room temperature drying, hot air drying, UV irradiation, infrared irradiation, etc.

[0026] The thickness of the layer to prevent accumulation of snow and ice on the surface of the substrate film depends on the type or size of the structure to be protected, the position of the parts, etc. However, it should be in the range of 1 to 200  $\mu\text{m}$ . If the thickness is less than 1  $\mu\text{m}$ , this layer is easily damaged or peeled off, and prevention of accumulation of snow and ice is difficult. On the other hand, if it exceeds 200  $\mu\text{m}$ , the adhesive film for preventing accumulation of snow and ice lacks flexibility. Therefore, an especially good range is 5 to 50  $\mu\text{m}$ .

[0027] The removable adhesive layer can be applied by adding a slight pressure for a short time at ambient temperature. Since it has cohesive force and elasticity, this layer can be released from a hard, flat, smooth surface even though it adheres strongly. Suitable adhesives should have adhering strength in the range of 10 g/25 mm to 1000 g/25 mm. The adhering strength of the adhesive is tested according to JIS Z0237 as follows. Adhesive is applied on one side of a 25 mm wide and 150 mm long sample, and the sample is laminated to another 25 mm sample. After compressing them, they are pulled apart in a tensile tester at  $300 \pm 30$  mm speed with a 150 mm gauge length. The strength (g/mm) of the adhesive is sought.

[0028] If the adhering strength is less than 10 g/25 mm, the bond is too weak, and the adhesive film is easily removed from structures where it has been applied, which is not desired. On the other hand, if it exceeds 1000 g/25 mm, the bond is too strong and the adhesive layer is hard to remove from the substrate film and from structures where it has been applied, and adhesive remains on both. When the adhesive film is replaced, adhesive remaining on the surface of the structure is hard to remove, and a lot of work is required to remove it completely.

[0029] Suitable adhesives include synthetic rubber based adhesives, acryl based adhesives, etc. Examples of synthetic rubber based adhesive include styrene-isobutylene-styrene block copolymers, styrene-butadiene-block copolymers, styrene-ethylene-butylene block copolymers, hydrogenated forms of these block copolymers, etc. The bond strength and durability of these synthetic rubber based adhesives can be adjusted by adding a tackifier, anti-aging agent, softening agent, etc. Suitable tackifiers include rhodine, denatured rhodine, petroleum resin, terpene resin, etc. Softening agent include plasticizers, polybutene, etc.

[0030] One example of a suitable acryl base adhesive has alkyl ester acrylate as its main component. It is co-polymerized with other monomer components. Alkyl ester acrylates include butyl acrylate, 2-ethyl hexyl acrylate, etc. Physical properties of the acryl base adhesive such as initial tackiness, bond strength, and restoring strength can be changed a great deal by co-polymerizing it with other monomers, changing the ratio, crosslinking molecules, etc. Monomers suitable for co-polymerization include vinyl acetate, acrylonitrile, acryl amide, styrene, methyl methacrylate, methyl acrylate, etc. Suitable acryl based adhesives include solution types and emulsion types. Either type can be used.

[0031] Methods of forming the adhesive layer on the back side of the substrate include (1) applying adhesive to the back side of the substrate and flashing the solvent or moisture; (2) applying adhesive to the release sheet, flashing the solvent, and applying it to the back side of the substrate, etc. The above method (1) can be used to form the layer that prevents accumulation of snow and ice. When method (2) is used, the adhesive layer is transferred to the substrate when the release sheet is removed. This release sheet can be used as a release sheet of product adhesive film without peeling.

[0032] The adhesive can be transparent or colored. In order to flash solvent and moisture from the adhesive, conventional methods such as ambient temperature drying, hot air drying, UV irradiation, infrared irradiation, etc. can be used. In order to increase the bond strength between the substrate film and adhesive, processes such as a primer coating, corona discharge treatment, UV irradiation, etc. should be used.

[0033] A release sheet is formed on the surface of the removable adhesive layer above. This release sheet protects the adhesive layer until it is applied to the surface of various structures. A material with flexibility and which can be easily removed from the adhesive layer is desired. In order to improve removal of the release sheet from the adhesive layer, a mold-release agent such as silicon can be applied to the surface which contacts the adhesive layer. This release sheet can be either film or paper. Its thickness can be in the range of 5 to 300  $\mu\text{m}$ .

[0034] The adhesive film for preventing accumulation of snow and ice according to this invention is explained above. It can be wound into a roll or laminated as a flat body with a fixed area and transported to the structures to be protected. It is applied to the areas that

require prevention of snow and ice accumulation. The adhesive film for preventing accumulation of snow and ice according to this invention is flexible, so it is easy to apply to curved surfaces, and it has superior workability. In addition to applying this invention directly to the surface to be protected from accumulation of snow and ice, it can be applied to metal wire on the surface. When this adhesive film for preventing accumulation of snow and ice is removed from the site where it has been applied, the adhesive layer remains attached to the substrate. Since no adhesive remains on the protected object, removal is easy.

[0035] Structures which can be protected by this film include bridge girders, bridge arches, buildings, roofs, electric wires, iron towers for wiring, ships (radar, bridge, life guard device), aircraft (wing, cargo, drain), marine structures (buoys, drilling rigs), railroads (lower portion of vehicles, track steps, pantographs), communication (various antenna, radar), traffic (signs, signals). Suitable structures are not limited to the above examples only.

[0036] In the following, this invention is going to be explained in detail based on example of practice. However, this invention is not restricted to the following examples.

[0037]

(Example of practice 1)

100 weight parts of a resin mixture which consists of 70 wt % of fluorine based copolymer resin with monomer components of 68 wt. % vinylidene fluoride, 30 wt. % of tetrafluoroethylene, 2 wt. % of hexafluoro propylene, and 30 wt. % of polymethyl methacrylate were dissolved in a mixed organic solvent which consists of 100 wt. parts of cyclohexanone, 60 wt. parts of butyl acetate, and 40 wt. parts of methyl isobutyl ketone. Next, the organic solvent solution of this mixed resin was augmented with 10 wt. parts of perfluoro alkyl carbonate (fluorine base surfactant). After mixing sufficiently in a ball mill to dispersing the components, a mixture for forming the layer to prevent accumulation of snow and ice was acquired. This mixture was applied to the surface of a hard polyvinyl chloride film with 50  $\mu\text{m}$  thickness by reverse coating. It was dried for 15 minutes in a hot air drier at 40°C, and a layer to prevent accumulation of snow and ice with 15  $\mu\text{m}$  thickness was formed.

[0038] The back side of the hard type polyvinyl chloride film above was coated with an acryl based adhesive (bond strength : 350 g/25 mm) with 2-ethyl hexyl acrylate as its main component by reverse coating, and an adhesive layer with 50  $\mu\text{m}$  thickness was formed. The surface of this adhesive layer was covered by a polyethylene film with 15  $\mu\text{m}$  thickness which had been coated with a silicone mold release agent. The adhesive film to prevent accumulation of snow and ice shown in section in figure 1 was acquired. In the figure 1, 1 is the plastic substrate, 2 is the layer to prevent accumulation of snow and ice, 3 is the adhesive layer, and 4 is the mold release sheet. This adhesive film to prevent accumulation of snow and ice was evaluated according to the following method. Results are shown in table 1.

[0039]

(Example of practice 2)

Example of practice 2 was the same as example of practice 1, except that substrate film was a soft polyvinyl chloride film. Similar procedures were used, and a layer to

prevent snow and ice from depositing, an adhesive layer, and a mold release sheet were formed. An adhesive film for preventing accumulation of snow and ice was acquired. This adhesive film to prevent accumulation of snow and ice was evaluated according to the following method. Results are shown in table 1.

[0040]

(Example of practice 3)

Example of practice 3 was the same as example of practice 1, except that, in addition to the fluorine based surfactant, 100 wt. parts of low molecular weight tetrafluoroethylene resin with 6.0  $\mu\text{m}$  average particle diameter and 8000 average molecular weight measured by the melting point method were added. Similar procedures were followed, and a layer to prevent accumulation of snow and ice, an adhesive layer, and a mold release sheet were formed. An adhesive film for preventing accumulation of snow and ice was acquired. This adhesive film to prevent accumulation of snow and ice was evaluated according to the following method. Result are shown in table 1.

[0041]

(Example of practice 4)

Example of practice 4 was the same as example of practice 3, except that the substrate film was changed to soft polyvinyl chloride, and in addition to the fluorine base surfactant, 100 wt. parts of low molecular weight tetrafluoroethylene resin (same as used in example of practice 3) was added. Similar procedures were followed, and a layer to prevent accumulation of snow and ice, an adhesive layer, and a mold release sheet were formed. An adhesive film for preventing accumulation of snow and ice was acquired. This adhesive film to prevent accumulation of snow and ice was evaluated according to the following method. Results are shown in tables 1 and 2.

[0042]

(Example of comparison )

The surface of a 50 cm x 50 cm square aluminum plate with 2 mm thickness was coated with a 50  $\mu\text{m}$  thick tetrafluoroethylene resin film using the same kind of adhesive layer as in example of practice 1. This was evaluated according to the following method. Results are shown in table 1.

[0043]

(evaluation test 1 of the area where snow accumulates)

The five films from the examples of practice and example of comparison were cut into 50 cm x 50 cm squares. Next, these squares were adhered to the surface of a 50 cm x 50 cm square aluminum plate through the adhesive layer. This aluminum plate was mounted facing the north-west in an area with a large amount of snow (Sapporo City, Hokkaido). From December to March 1995, it was observed 24 hours a day by a video camera. Photographs were made every time snow fell, and the layer to prevent accumulation of snow and ice was divided into 100 sections. After observing snow accumulation, the amount of area where snow was deposited was determined, and the

sample's effectiveness in preventing accumulation of snow was evaluated. Smaller values of area where snow was deposited means there was less snow deposit.

[0044]

table 1

Number	Wind direction	Wind speed	Temperature (°C)	Area where snow was deposited				
				Ex. of pract 1	Ex. of pract 2	Ex. of pract 3	Ex. of pract 4	Ex. of comparison
1	NNW	1.2	-5.8	0	0	0	0	68
2	NW	3.6	-7.2	0	0	0	0	68
3	NNW	4.8	-6.0	0	0	0	0	33
4	N	3.6	-1.8	0	0	0	0	24
5	NW	6.6	-4.8	0	0	0	0	0
6	N	0	-0.2	0	0	0	0	100
7	NNW	6.6	1.8	0	0	0	0	0
8	NW	9.6	0.5	0	0	0	0	100
9	NW	6.6	0.8	0	0	0	0	90
10	NNE	6.6	1.8	0	0	0	0	5
11	NW	4.2	-1.0	0	0	0	0	68
12	NW	3.6	-0.8	0	0	0	0	0
13	NNW	1.2	-0.9	0	0	0	0	100
14	NNW	3	-1.6	0	0	0	0	100
15	NW	4.8	-6.5	0	0	0	0	84
16	NNW	0.6	-9.1	0	0	0	0	69
17	NW	0.9	-8.9	0	0	0	0	71
18	-	0	-8.6	0	0	0	0	77
19	N	0.6	-9.2	0	0	0	0	69
20	NNW	3	-1.0	0	0	0	0	100
21	NNW	3	-3.8	0	0	0	0	5
22	NW	3	-4.7	0	0	0	0	41
23	NW	5.4	-10.3	0	0	0	0	59
24	W	2.4	-8.5	0	0	0	0	56
25	W	2.4	-8.5	0	0	0	0	53

[0045]

table 2

Number	Wind direction	Wind speed	Temperature (°C)	Area where snow was deposited				
				Ex. of pract 1	Ex. of pract 2	Ex. of pract 3	Ex. of pract 4	Ex. of comparison
26	WNW	3.6	-11.6	0	0	0	0	80
27	NW	4.8	-11.4	0	0	0	0	81
28	NNW	3	-7.1	0	0	0	0	44
29	W	1.2	-3.8	0	0	0	0	43
30	SW	3	-8.4	0	0	0	0	39
31	NW	4.2	-5.4	0	0	0	0	26
32	SSW	0.6	-8.2	0	0	0	0	67
33	-	0	-7.7	0	0	0	0	70
34	WNW	1.2	-6.3	0	0	0	0	46
35	W	1.2	-8.3	0	0	0	0	48
36	ENE	0.6	-10.2	0	0	0	0	48
37	ESE	1.2	-10.1	0	0	0	0	48
38	NW	1.2	-9.0	0	0	0	0	41
39	NNW	0.6	-9.1	0	0	0	0	0
40	E	0.6	-8.1	0	0	0	0	6
41	ENE	1.8	-3.9	0	0	0	0	26
42	NNW	4.2	0.3	0	0	0	0	25
43	N	11	-0.2	0	0	0	0	81
44	NNW	4.2	0.4	0	0	0	0	0
45	NW	6	-4.0	0	0	0	0	65
46	NNW	5.4	-1.9	0	0	0	0	0
47	N	2.4	-2.6	0	0	0	0	100

[0046]

From table 1 above, while there was no confirmed snow deposits on the adhesive film for preventing accumulation of snow and ice according to this invention (refer to example of practice 1 to 4) over a wide temperature range of 1.8 to -11.6°C and wind speeds of 0 to 11 m/sec., it was obvious that snow deposits were considerable in the example of comparison.

[0047]

(evaluation test 2, snow deposits on road signs)

The four adhesive films for preventing accumulation of snow and ice from examples of practice 1 to 4 were applied to existing road signs. Snow deposits on signs where the films had been applied and signs where these were not applied were observed, and the condition of snow deposits was observed. On signs where film from example of practice 1 to 4 had been adhered, there were no confirmed snow deposits. However, signs where this film was not applied has intense snow deposits, and the traffic signs could not be read.

[0048]

(evaluation test 3, release of the adhesive layer)

The adhesive film for preventing accumulation of snow and ice from example of practice 1 and the adhesive film for preventing accumulation of snow and ice from the example of comparison were applied to the surface of a stainless steel plate following JIS Z0237. Bond strength was measured according to JIS Z0237 after 20 minutes and after 1 day. They were left outside for 4 months during winter and then removed from the stainless steel plate. The condition of the adhesive layer was observed visually. The results of this observation and the bond strength results are shown in table 3 below.

[0049]

table 3

Number	Kind of film	Adhering strength (g/25 mm)		Result of peel test (after leaving outside for 4 months)
number		After 20 min	After 1 day	
Evaluation test 3-1	Adhesive film of example of practice 1	210	350	No adhesive remained on the surface of the steel plate.
Evaluation 3-2	Adhesive film of example of comparison	1200	3100	Large amount of adhesive remained on the surface of steel plate, and the substrate film was damaged.

[0050]

(Effects of this invention)

This invention has especially advantageous effects as follows, and its industrial value is extremely high.

1. This adhesive film to prevent accumulation of snow and ice according in this invention can be applied to the surface of various structures where accumulation of snow and ice is to be prevented. Compared to the former method of coating, it is hardly affected by weather and can be applied without any special skill. The work is simple.
2. The adhesive film to prevent accumulation of snow and ice according to this invention is effective in preventing accumulation of snow and ice over a wide temperature range from 0°C to -10°C since a layer to prevent accumulation of snow and ice containing a certain amount of specific hydrophobic organic substances is formed on the surface of substrate film.

3. Since the adhesive film to prevent accumulation of snow and ice according to this invention has a removable adhesive layer on the back side of the substrate, when it is repaired, removal is easy, and reapplication can be done easily.

(Simple explanation of figures)

Figure 1: cross section of the adhesive film to prevent accumulation of snow and ice according to this invention.

(Explanation of symbols)

- 1: plastic substrate film
- 2: layer to prevent accumulation of snow and ice
- 3: adhesive layer
- 4: mold release sheet

Amendment

(submitted date) Dec. 2, 1996

(amendment 1)

(name of document of object of amendment) Detailed report

(name of item of object of amendment) simple explanation of figures

(amendment method) change

(contents of amendment)

(Simple explanation of figures)

Figure 1: cross section figure of the adhesive film to prevent accumulation of snow and ice according to this invention.

(Explanation of symbols)

- 1: layer to prevent accumulation of snow and ice
- 2: plastic substrate film
- 3: adhesive layer.
- 4: mold release sheet